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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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ABSTRACT

A gas-blending system was constructed for producing hydrogen fluoride-air mixtures in the concentration range from 1 to 20 ppm for the purpose of calibrating analytical monitoring devices. The system has been tested by measuring these HF concentrations using a fluoride ion-specific electrode.

1. INTRODUCTION

A gas dilution system was constructed which permits the dilution of relatively high concentrations of hydrogen fluoride in air to known low concentrations in the range from 1 to 20 ppm. The high concentration bulk mixture and diluent air are mixed in a chamber at accurately controlled flow rates. The diluted mixture then passes to a sampling manifold where the known concentration of HF in air can be sampled or analyzed. The sampling manifold can be directly attached to a collector or other device for purposes of monitoring the HF concentrations produced.

2. EXPERIMENTAL

2.1 Description of Dilution System

Figure 1 shows a schematic diagram of the dilution system. The HF working standard is admitted into the system through a stainless steel (s.s.) ON-OFF valve (V-1). The flow rate is established with a s.s. differential flow rate controller (DFC-1) and a s.s. flow control valve (FCV-1). The flow rate is measured with a plastic bodied rotameter (constructed of acrylic material). Similarly, the diluent air is admitted into the system and mixed in the mixing chamber with the HF bulk mixture. This system is designed to produce dilutions from zero to a hundredfold of the HF bulk mixture. For determina-

tion of the HF concentration in the manifold, a sample is taken, using a s.s. absorption tube and analyzed with a fluoride-ion selective electrode analytical system. The metal components for the diluent air are constructed of brass and 1/4" o.d. copper tubing. The regulator used on the HF bulk mixture cylinder is constructed of non-corrosive Monel metal. The mixing chamber, sampling manifold, and all tubing connections on the HF side of the dilution system are constructed of stainless steel. Photographs of the dilution system are shown in Figures 2 to 4.

2.2 Description of Analytical System

The HF concentrations are determined by passing a known volume of the mixture through a known quantity of 0.1 M NaOH. The HF is rapidly neutralized to form NaF. The fluoride-ion concentration of the resulting solution is measured with a fluoride ion-selective electrode.

The apparatus consists of an ion-selective electrode, a calomel reference electrode, a glass electrode for measuring the pH of the solution, and a pH meter. A schematic diagram of the apparatus is shown in Figure 5.

The glass electrode is necessary for adjusting the pH of the NaOH absorbing solution. Below pH = 4 the NaF hydrolyzes to form undissociated HF yielding low results. Above pH 8, hydroxyl ion interferes and yields high results. The glass electrode is disconnected after the pH adjustment and the fluoride-ion concentration is measured with the same meter, using the ion-selective electrode.

2.3 Calibration of Measurement System

The ion-selective electrode was calibrated with standards prepared as follows:

A 0.0500 M stock solution of NaF was prepared by dissolving 2.100 grams of reagent-grade NaF, previously dried at 110 °C, in distilled water in a 1 liter volumetric flask. Standard solutions from 1.00×10^{-2} to 1.00×10^{-5} M were prepared by accurate dilution of the stock solution with 0.1 M KNO₃ in

100-ml volumetric flasks. The KNO_3 is used to maintain the same ionic strength as the 0.1 M NaOH absorbing solution. The NaF solutions are stored in polyethylene containers. Figure 6 shows a typical calibration curve. These solutions were measured periodically and the millivolt readings obtained are presented in Table 1.

Table 1
Stability of Calibrating Solutions

<u>Concentration</u>	<u>Date, 1973</u>	<u>Millivolts</u>
$1.0 \times 10^{-5} \text{ M}$	4/3	+127.4
	4/7	+125.8
$1.0 \times 10^{-4} \text{ M}$	4/3	+67.6
	4/7	+66.3
	4/30	+66.0
	4/3	+7.5
$1.0 \times 10^{-3} \text{ M}$	4/7	+7.0
	4/30	+6.3
	5/15	+7.5

These results indicate that a new calibration curve is not required every time a series of fluoride ion measurements are to be made. However, it is recommended that a calibration be performed with at least two solutions prior to the start of any fluoride ion measurements. This is particularly important if the electrode has not been used for several weeks.

2.4 Preparation of HF-air Bulk Mixture

To evaluate the dilution system it was desirable to prepare an HF bulk mixture in the range from 50 to 100 ppm. This was done by adding 200-220 mm Hg pressure of hydrogen fluoride vapor from a cylinder of liquid hydrogen fluoride to a large evacuated cylinder. Air was then added to a pressure of 1000 psi. Subsequent analysis by the method described in Section 2.5 yielded an average concentration of 61 ppm. The difference in concentration behavior predicted, 4000 ppm, and the observed value is due to reactor of some HF with the cylinder material or with foreign materials with the cylinder.

2.5 Procedure for Measuring HF-Air Mixtures

The hydrogen fluoride concentration of the bulk mixture was determined as follows:

15.0 ml of 0.1 M NaOH was added to the collection tube which was then connected to the dilution system. The exhaust end of the collection tube was connected to a wet-test meter and the diluent air control (V-2) turned to the "off" position. An accurately measured volume of 10 to 20 liters was bubbled through the 0.1 M NaOH solution at a rate from 0.5 to 1.0 l/min. Valve V-1 was turned off, and the solution was transferred to a 50-ml polyethylene beaker. The pH of this solution was adjusted to values between 5.5 and 6.5 with three drops of concentrated nitric acid followed by dropwise addition of 1:1 nitric acid. The pH meter was calibrated in this range using a standard buffer. No volume dilution correction was made if the added acid did not exceed four drops (i.e. about 0.2 ml). The fluoride-ion concentration, C_F , of this solution was then measured, allowing about 5 to 10 minutes for the electrode reading to stabilize. The concentration of the solution was determined by reference to the calibration curve in Figure 6.

The concentration of hydrogen fluoride, $C_{HF}(\text{ppm})$, in a gaseous mixture is calculated by the relationship

$$C_{HF}(\text{ppm}) = \frac{C_F \ v \ E}{1000V} \times 10^6$$

where C_F = fluoride ion concentration (from ion-selective electrode measurement) (mol/l).

v = volume of test solution (ml).

V = volume of gas sampled (l).

E = molar volume of gas (24.5 l at 25 °C and 760 mm).

The concentration of HF in the diluted gas was determined similarly, except the sampling is done from the manifold.

2.6 Stability Study of HF Bulk Mixtures

In order to use the dilution system described herein effectively it is essential to have a bulk mixture where the concentration remains unchanged over a reasonable period of time. For this reason the HF bulk mixture was analyzed periodically over a period of several weeks. Results of measurements over a 6-week period are plotted in Figure 7, together with the mean value of all determinations. No significant decrease in the HF concentration level occurred during this 6-week interval.

3. EVALUATION OF THE PERFORMANCE OF THE GAS DILUTION SYSTEM

Various dilute mixtures in the range of 1 to 20 ppm were prepared by mixing the bulk mixture with diluent air at measured flow rates. A summary of the measurements made are tabulated in Table 2.

Table 2
Summary of Calculated and Observed HF
Concentrations

Bulk Mixture Flow Rate 1/min	Air Flow Rate 1/min	Dilution Factor	HF Conc. Calc'd,ppm	Average HF Conc. Obs.,ppm	Deviation Obs- Calc'd,ppm
0.272	0.500	0.3523	21.5	19.5(4)	-2.0
0.272	0.943	0.2239	13.7	11.6(5)	-2.1
0.109	0.411	0.2096	12.8	13.0(15)	+0.2
0.105	0.905	0.1040	6.3	5.3(9)	-1.0
0.050	0.503	0.0904	5.5	4.7(5)	-0.8
0.054	2.83	0.01869	1.1	1.1(4)	0

Columns 1 and 2 of Table 2 contain the measured flow rates from which the dilution factors in column 3 are calculated. The calculated HF concentrations, obtained by multiplying 61 ppm (i.e. the bulk mixture concentration) by the respective dilution factor are given in column 4. The mean observed HF concentrations, based on the number of fluoride determinations given in the parenthesis are tabulated in column 5. The last column is the difference between the observed and calculated HF values, in ppm. Examination of these results indicates that the measured values

are generally 10 to 20 percent lower than the calculated values. This is also demonstrated in Figure 8 where the slope of the solid line (measured values) is less than the predicted line (dotted line in figure).

Two factors may contribute to the imprecision of the results. The first involves analytical errors including collection efficiency. Physical or chemical adsorption of the HF in the dilution system may also be a problem. The latter would also account for the observed values being generally less than the calculated values.

The sample collection efficiency was evaluated by using two collection tubes in series, each containing 15 ml of 0.1 M NaOH. Fluoride analysis of each solution indicated that the HF collection efficiency in the first collection tube was better than 99 percent. The reproducibility of the analytical measurement was investigated by repeated measurements of fluoride standard solutions, and solutions obtained from the HF monitor of the dilution system. The relative standard deviation calculated from these results did not exceed 5 percent. Therefore, it appears that the analytical system is not the major cause of the imprecision.

To obtain more definitive information on the cause of the deviation between the observed and calculated values, experiments were performed in which the HF bulk mixture was analyzed under different conditions of flow rate. The results are plotted in Figure 9 and summarized in Table 3.

Another experiment was performed to further characterize this behavior. This consisted of preparing a bulk mixture in "super-dry" nitrogen at a 40 ppm HF concentration level and comparing the HF measurements from the manifold of the dilution system with measurements made directly from the cylinder as shown in Figure 10. Super-dry nitrogen was used to prepare this

TABLE 3

Observed Bulk Mixture Concentrations of HF for
Various Flow Rates and Collection Times

Experiment No.	Obs. HF Conc., ppm	Vol. Collected, Liters	Flow Rate ml/min.	Comments
1	12.3	18.0	400	No prior flushing of system with HF standard
2	37.7	21.0	300	System flushed with HF standard for 1-2 min. then sample 2 collected
3	59.5	21.0	923	Sample 3 collected at greater flow rate than sample #2
4	50.5	20.0	400	HF valve (V-1) turned off and sample #4 collected one hour after 3 with no prior flushing of system with HF standard
5	45.4	16.2	136	Flow rate decreased from 400 ml/min to 136 ml/min.
6	57.5	20.1	775	Flow rate increased from 136 ml/min. to 775 ml/min.
7	56.0	21.0	540	System flushed for 5 min. at 1.0 l/min before collecting 7 through 11
8	59.8	12.0	540	---
9	55.1	12.0	540	---
10	56.8	12.0	540	---
11	61.3	12.0	540	---

mixture in order to minimize any moisture in the cylinder (e.g. breathing air may contain as much as 50 ppm H_2O). A series of measurements was made as mentioned above and the results are shown graphically in Figure 11. The HF values indicated by A in the figure were measured as collected from the manifold of the dilution system after first flushing the system for five minutes at 3-4 liters/min. Group B represents the range of values measured directly from the tank via the Teflon impinger. Group C represents the range of values measured via the dilution system after first flushing the system for 20 minutes at 3-4 liters/min.

One conclusion that may be drawn from these experiments is that several hours of flow are necessary to establish a stable concentration in the system. The series of experiments 4, 5, 6 in Table 3 and indicated by a broken line in Figure 9 suggests that low flow rates may result in decreased concentrations in the manifold by an adsorptive or reactive means. A minimum flow rate of 500 ml/min appears to be required to maintain a stable concentration in the manifold. These results show that even after flushing the dilution system for 20 minutes (C in Figure 11) at a high flow rate the mean result is 13 percent less than the average found when using the Teflon impinger only.

The stability of the HF concentration generated over an eight hour working day, was investigated. This consisted of first flushing the dilution system for 20 minutes with the bulk mixture containing 61 ppm of HF at a flow rate of 0.7 l/min. The flow rate was then decreased to .109 l/min and diluent air was added at a flow rate of 0.411 l/min and mixed. The calculated dilution factor was 0.21. The HF concentration was measured 3 to 10 1/2 hours after the initial adjustment of the flow rate conditions. These results are plotted in Figure 12. The average value to be compared with a predicted value of 12.8 ppm was 14.2 ppm with a relative standard deviation of 0.8 ppm.

4. SUMMARY

In summary, the results indicate the feasibility of dilution of bulk mixtures to obtain concentrations in the 1 to 20 ppm range. An empirical formula can be written to correct for the observed bias between the measured and calculated HF values as follows:

$$C_d = k C_B \times D.F.$$

where C_d = the desired HF concentration level corresponding to a particular value of the dilution factor, C_B is the concentration of the bulk mixture, and k is the experimentally determined factor. For this particular dilution system, $k = 0.9$. However, it is recommended that users of this system periodically measure the concentration of a diluted HF sample using the fluoride-ion selective electrode analytical method to ensure accurate values. The analytical method requires only a minimum of experience and expertise to perform the measurements.

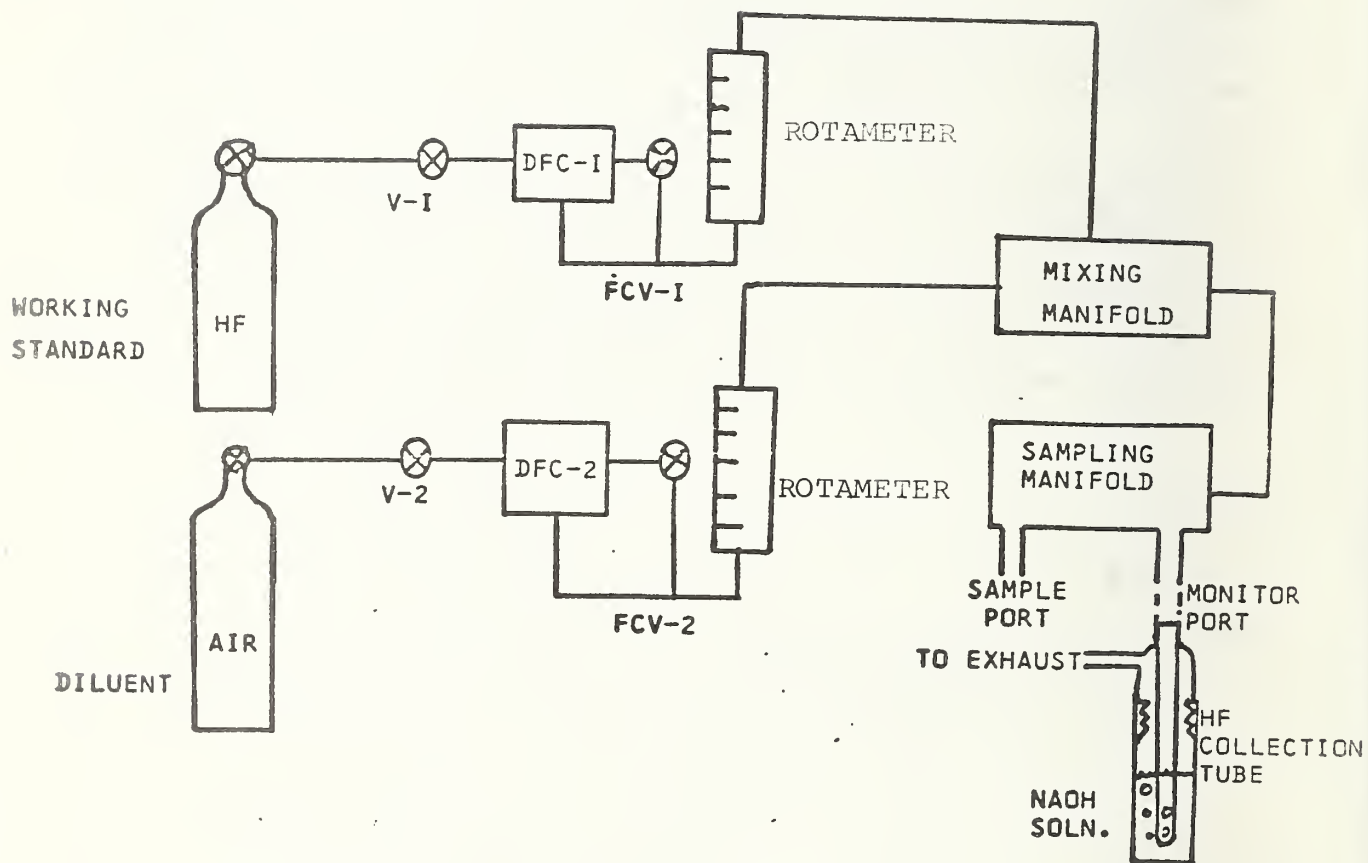


Figure 1. HF Dilution System.

GAS GENERATING SYSTEM
HF
310.05 NO. 3

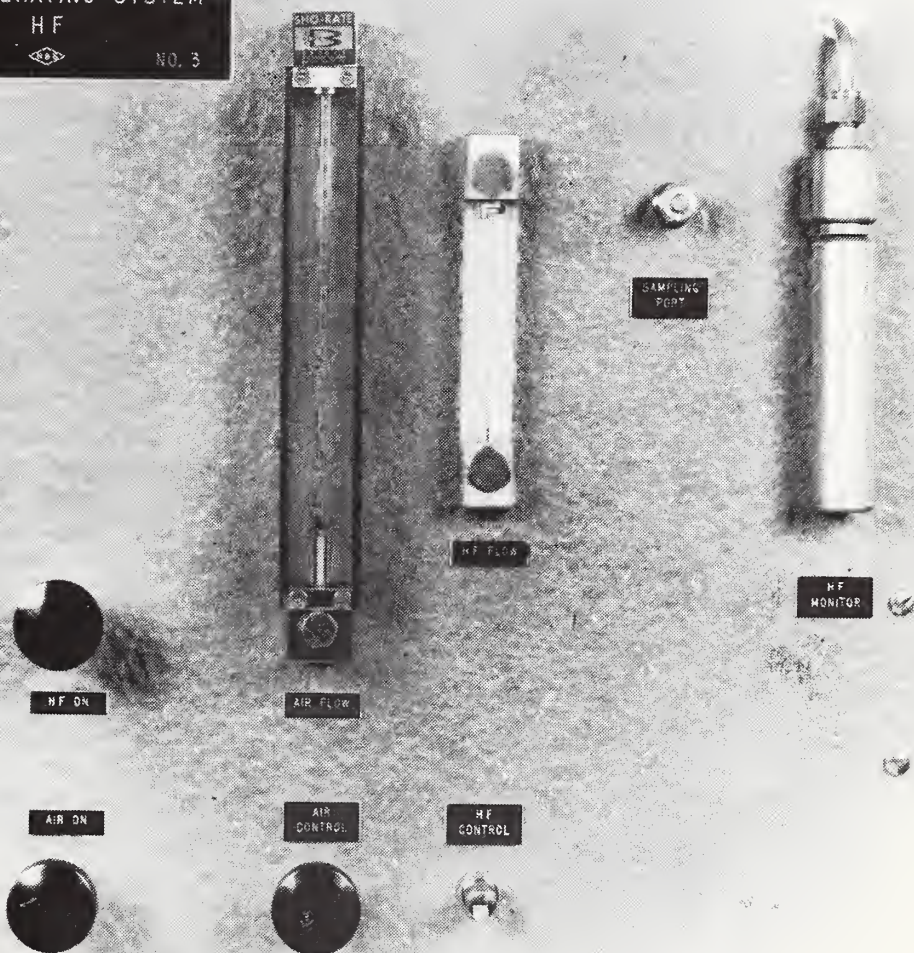


Figure 2. Front View of Dilution System.

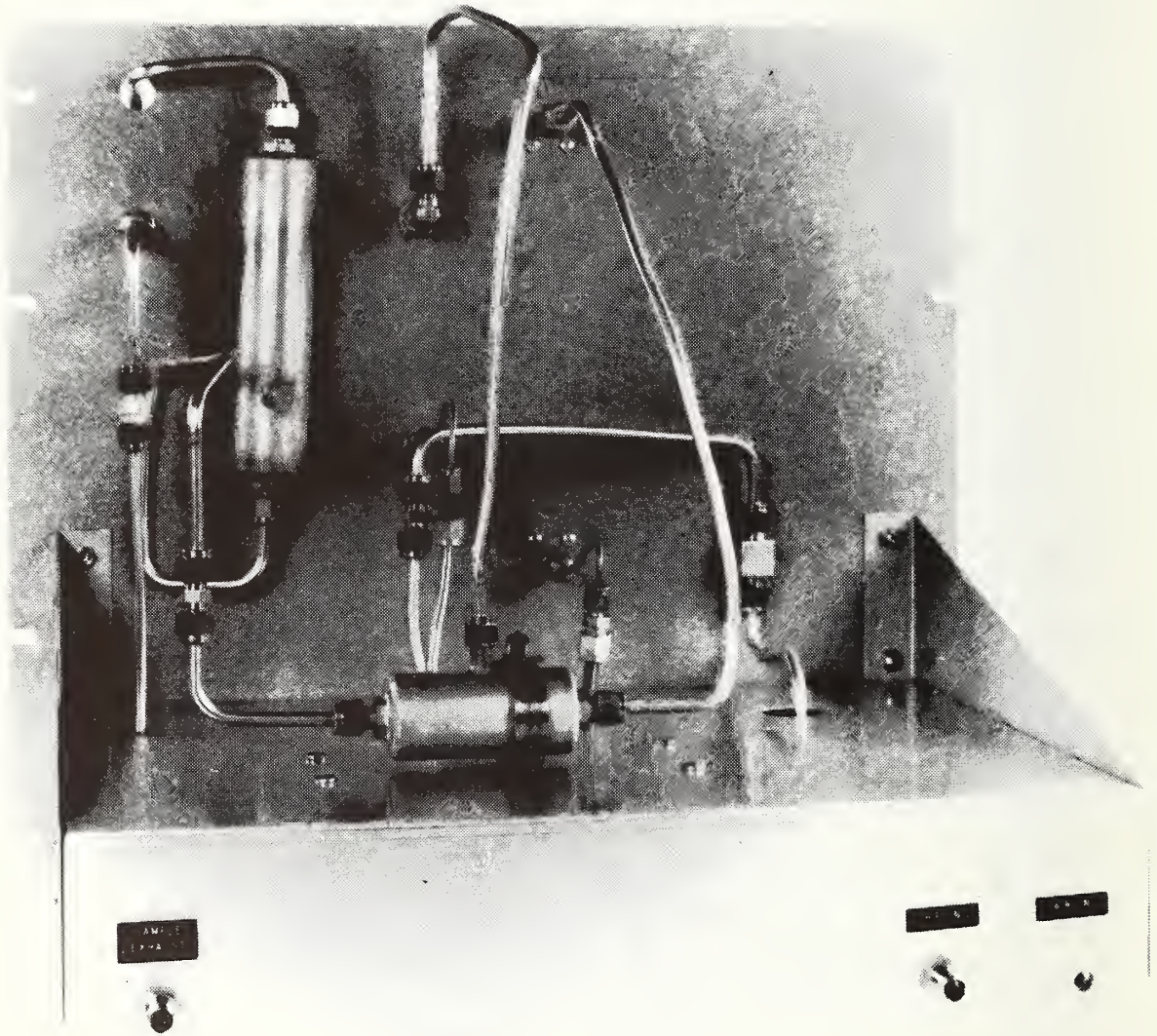


Figure 3. Rear View of Dilution System.

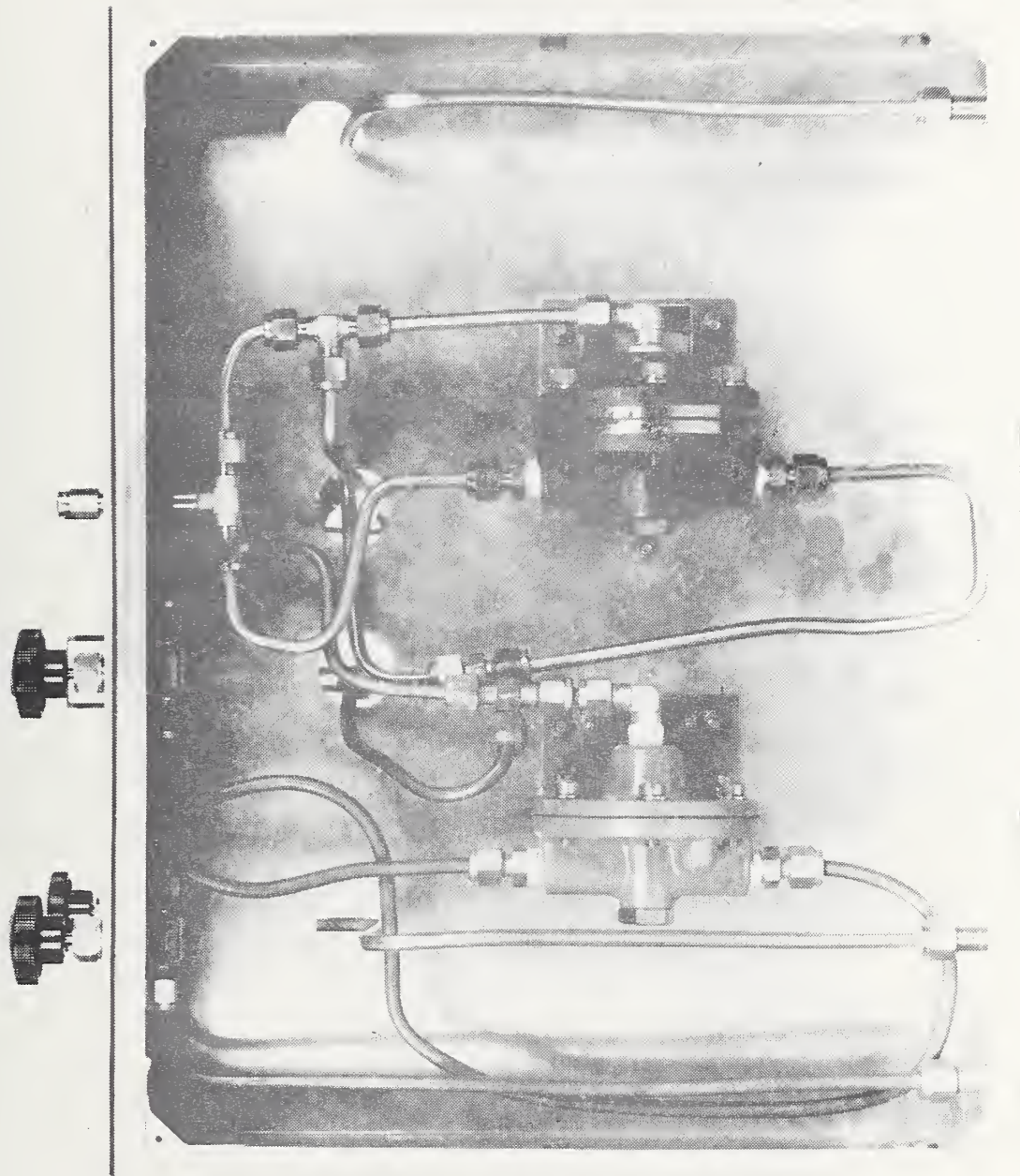


Figure 4. Bottom View of Dilution System.

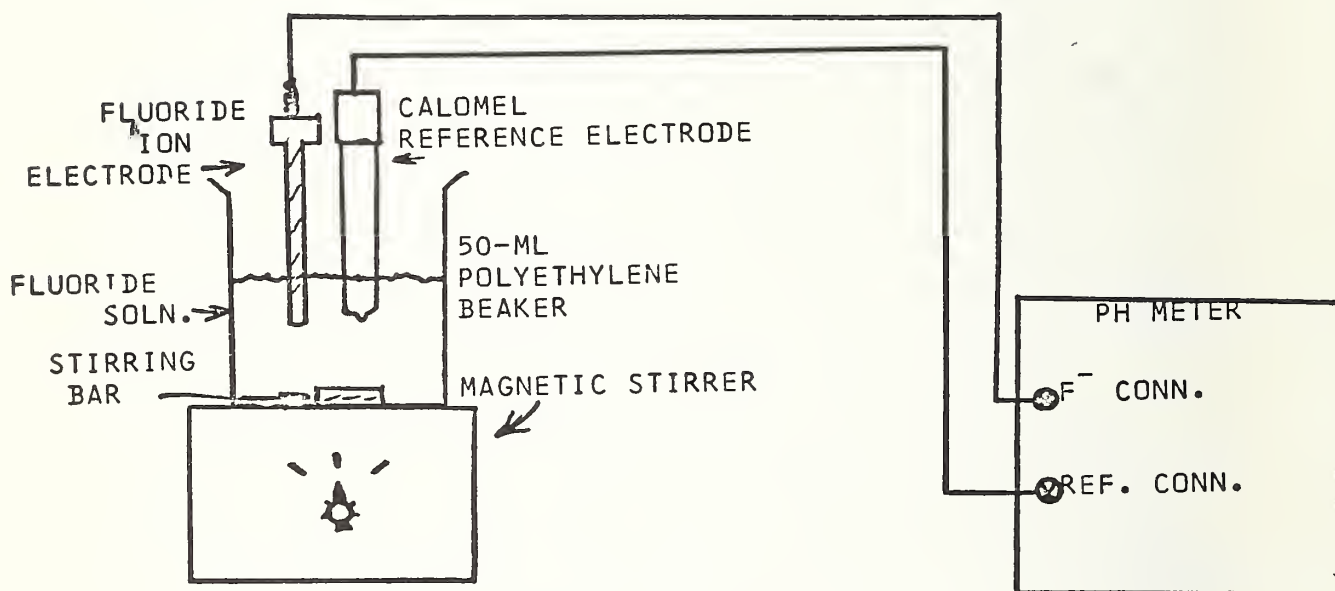


Figure 5. Apparatus for Fluoride Analysis.

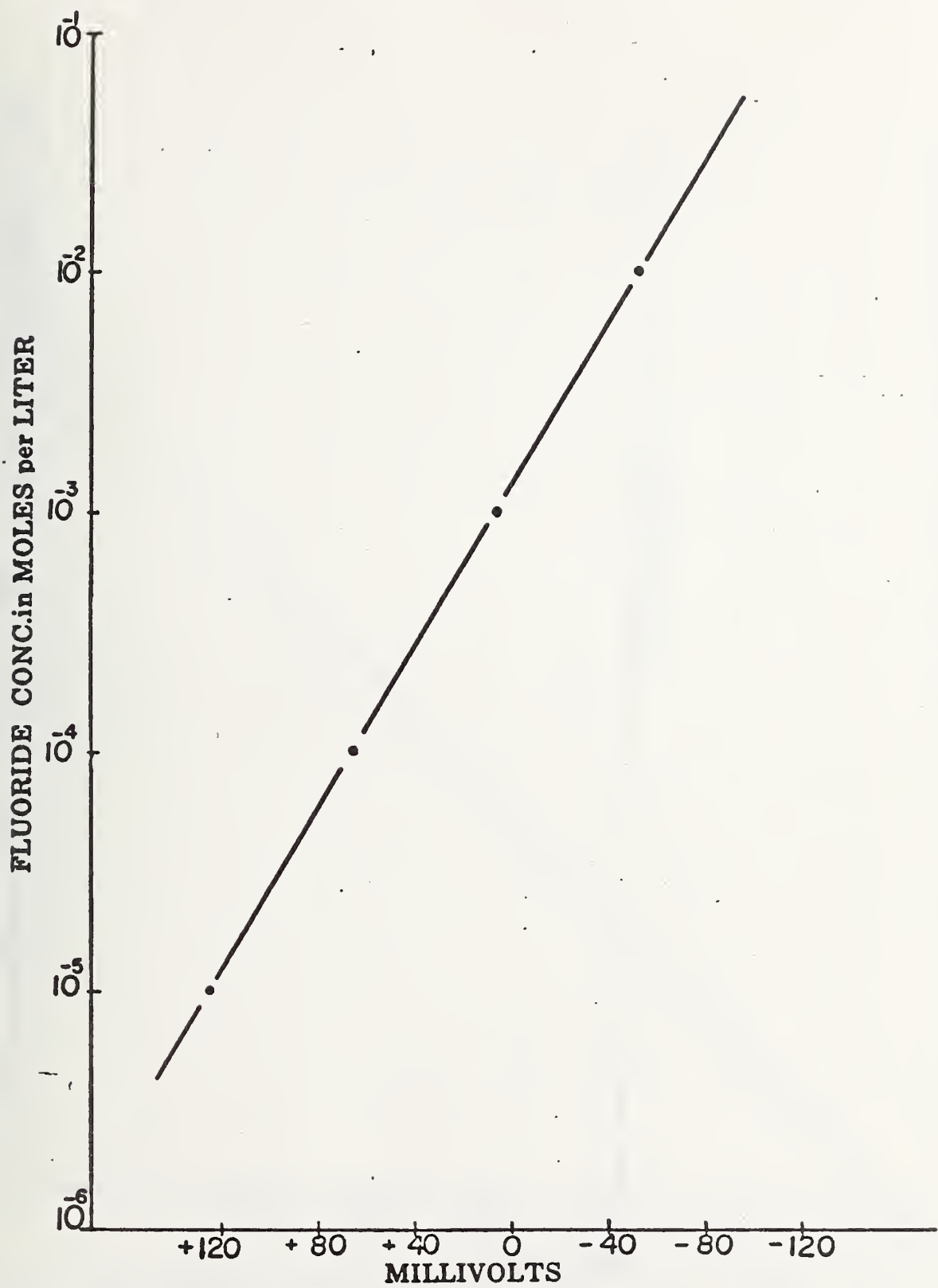


Figure 6. Calibration Curve for Fluoride Ion.

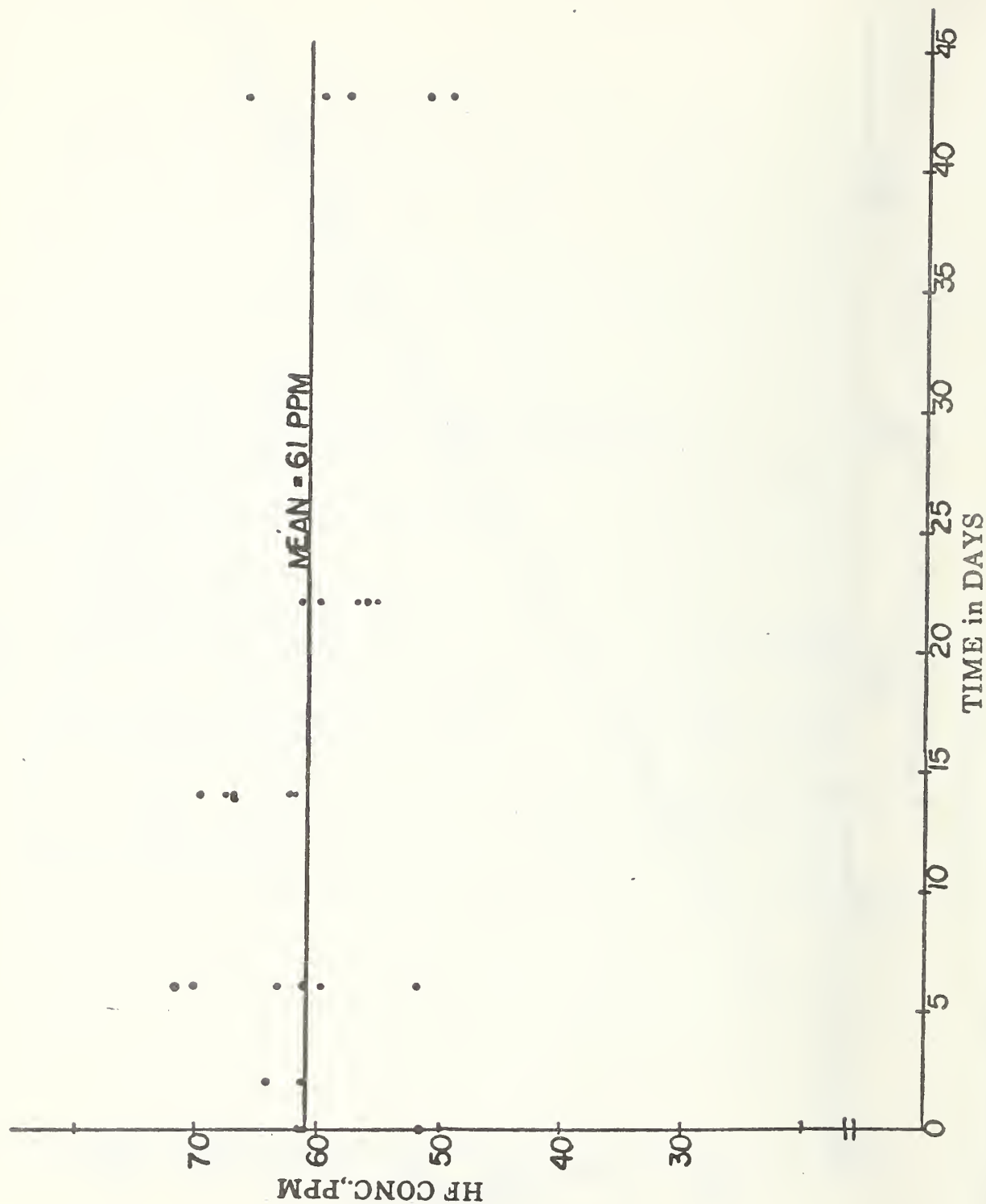


Figure 7. Observed HF Working Standard Concentration vs. Time.

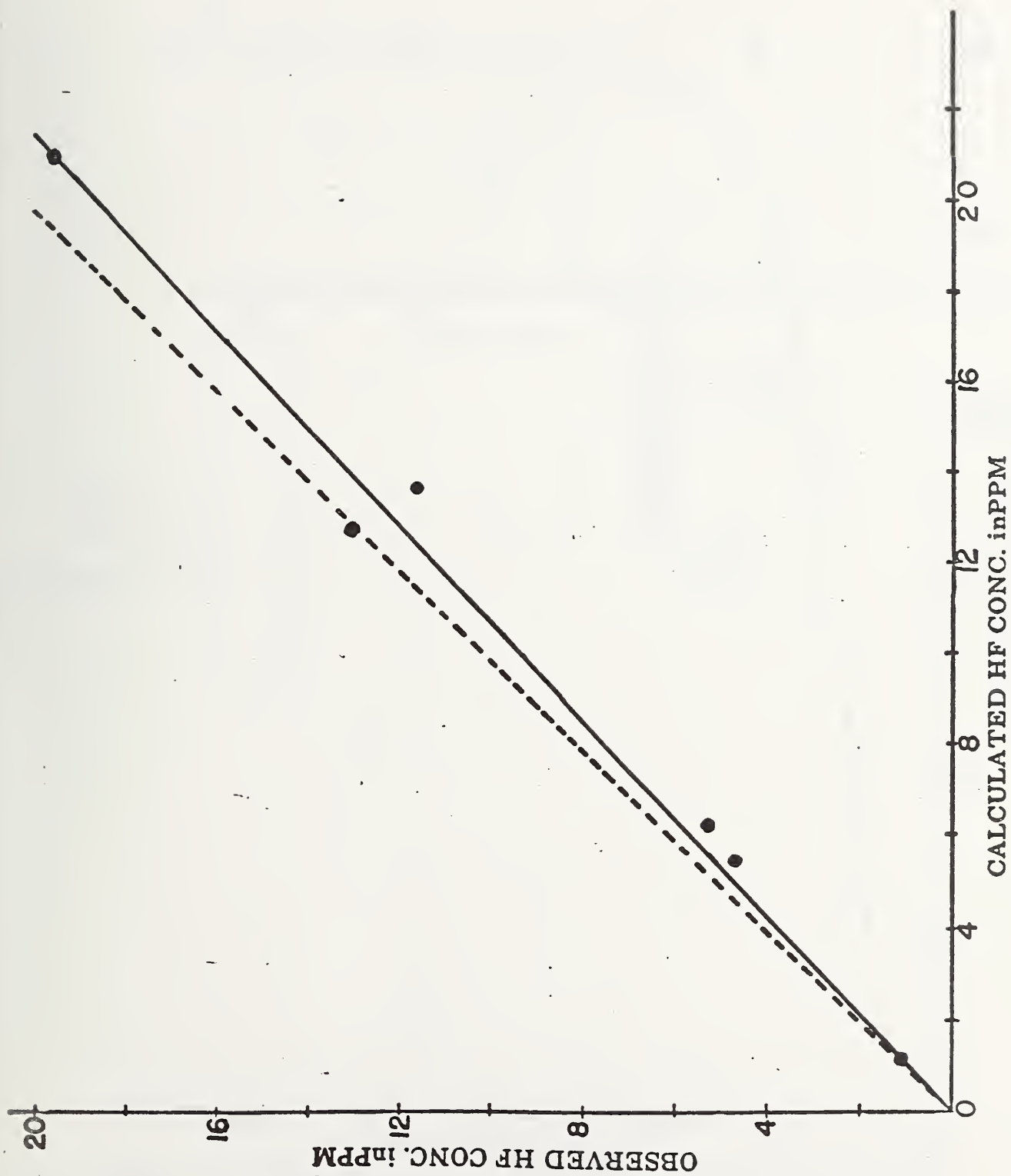


Figure 8. Observed vs. Calculated HF Concentration.

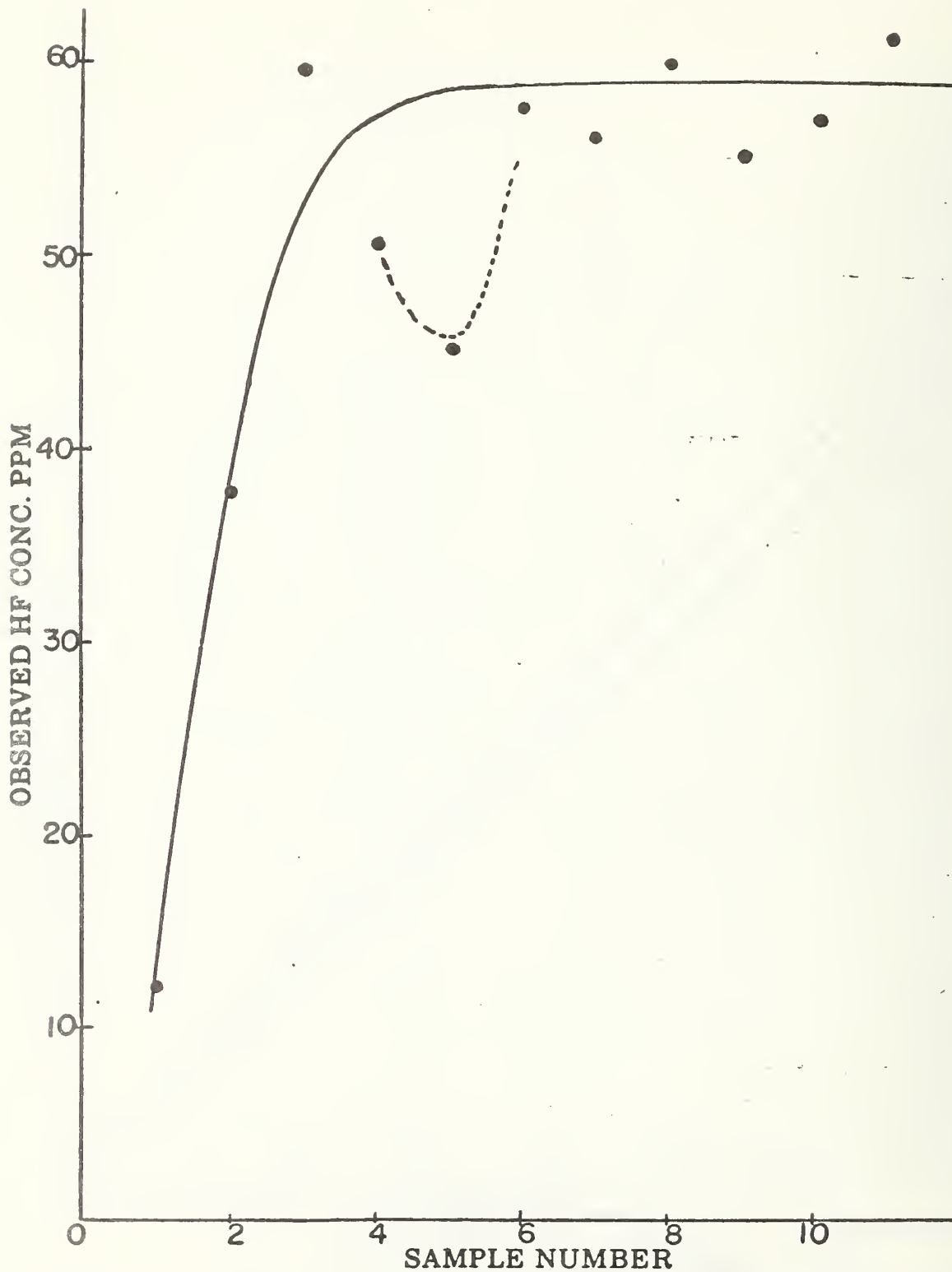


Figure 9. Concentration of HF Working Standard vs. Sample Taken (see Table 3).

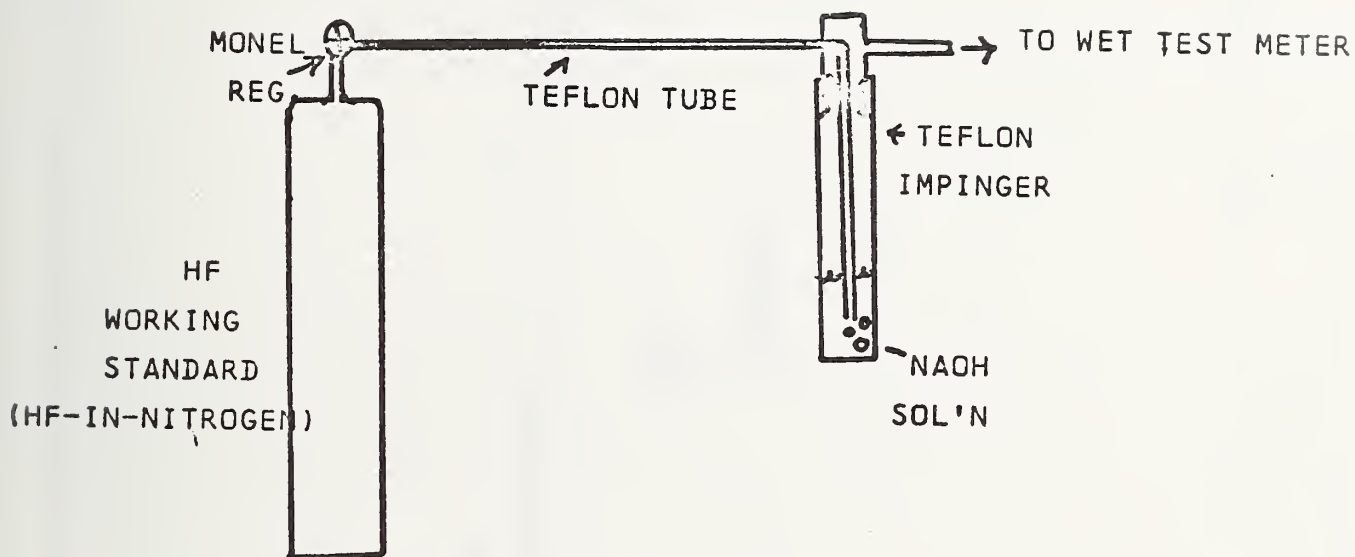


Figure 10. Measurement of HF Working Standard Via Teflon Impinger.

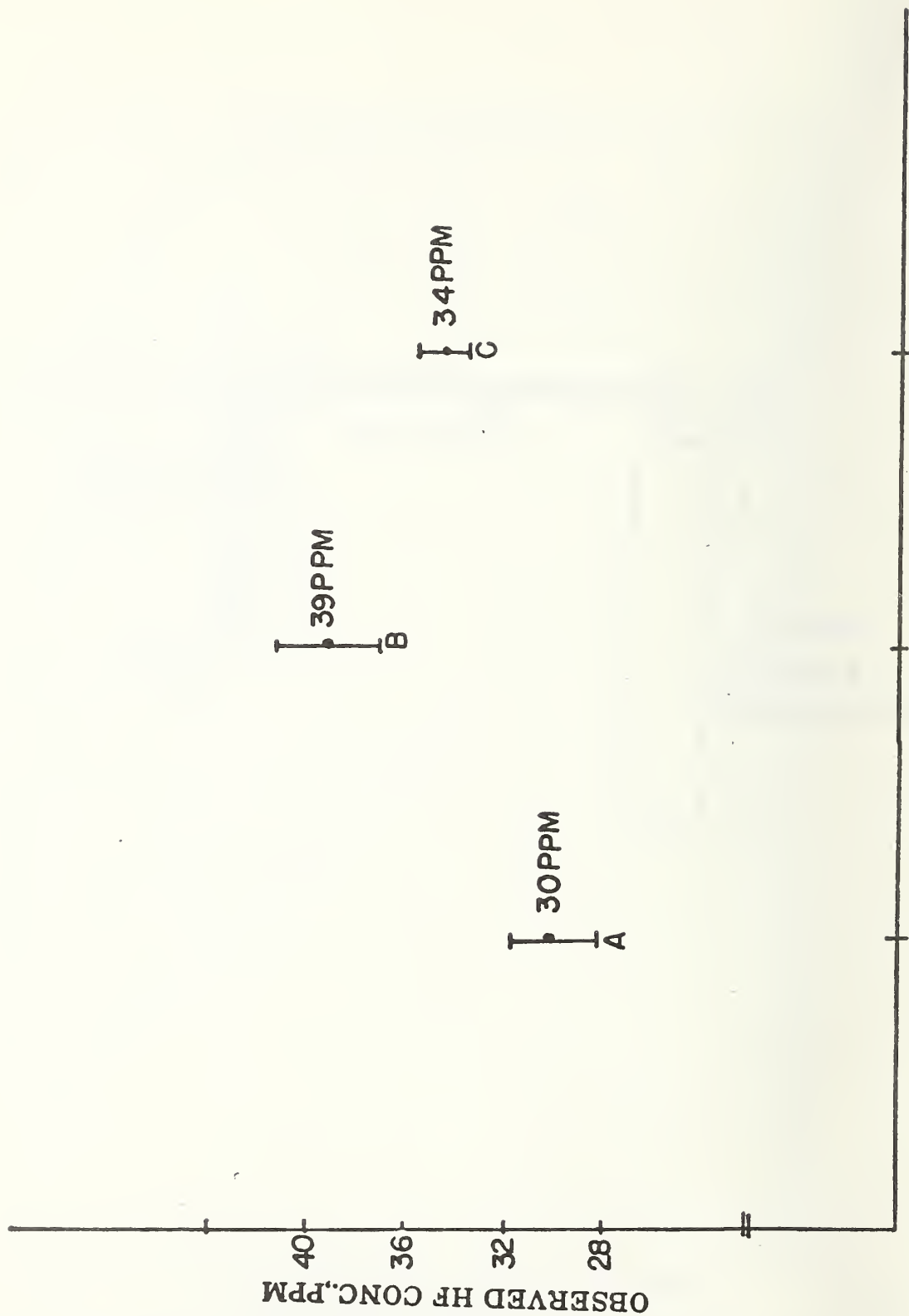


Figure 11. Comparison of HF Measurements.

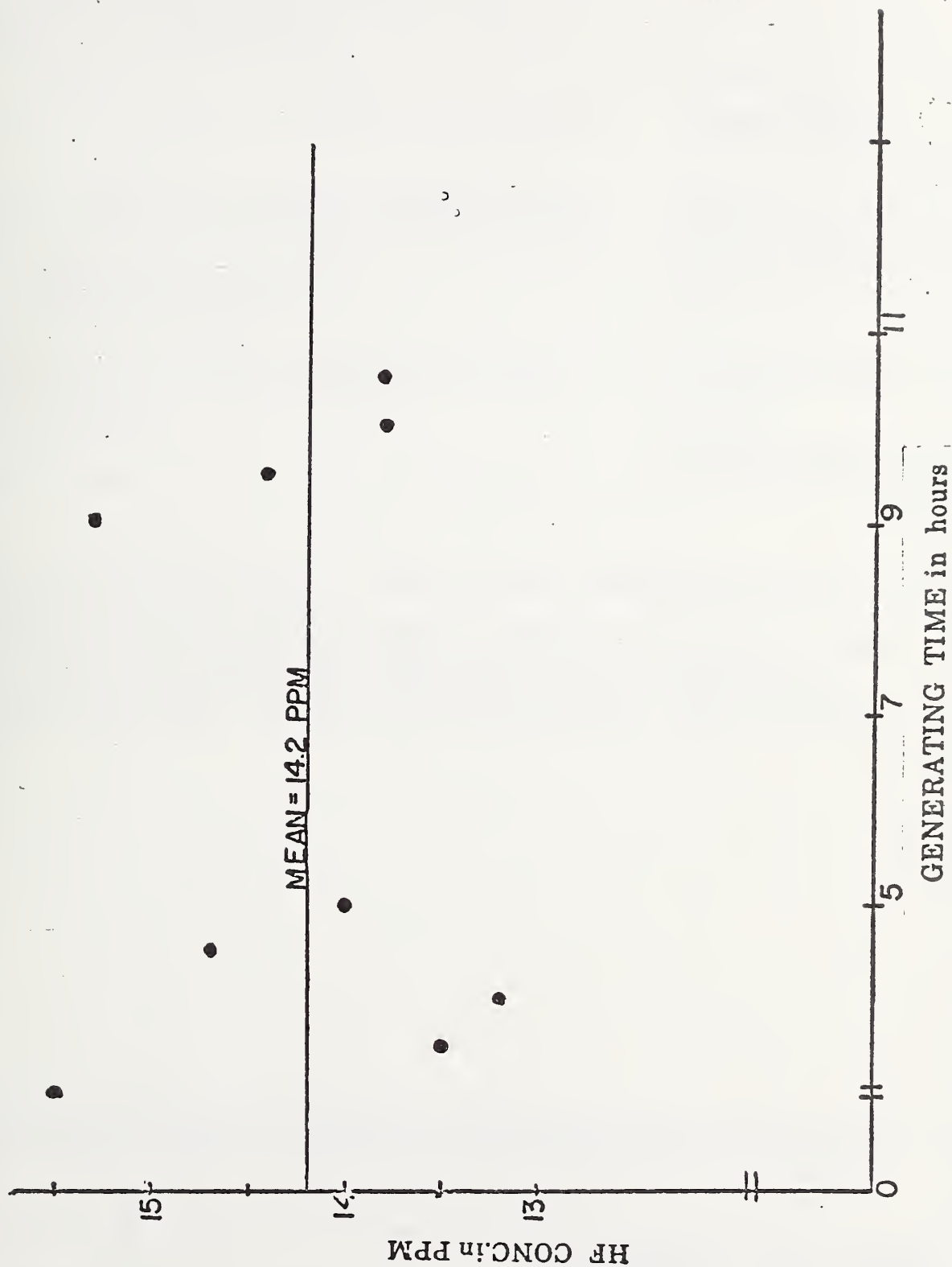


Figure 12. Observed HF Concentration vs. Generating Time.

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